

Studies on Biodegradability, Morphology and Mechanical Properties of Low Density Polyethylene/Sago Based Blends

Wan Aizan Wan Abdul Rahman, Roshafima Rasit Ali*, Naterah Zakaria

*Polymer Engineering Department, Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.*

Abstract

In this study, sago starch was physically blended with LDPE via two-roll mill to produce LDPE/sago starch (SS) biodegradable films. Glycerol was added to the blends as a plasticizer to increase the compatibility of sago starch and LDPE, which also subsequently reduced the brittleness of the film. Melt flow index of the blends was measured to determine the rheological properties and the viability of the blends to undergo blow film process. Gloss test was also studied to determine the optical properties. Mechanical and morphology studies of LDPE/SS biofilms have been done by tensile testing machine and microscopy respectively. Exposure of LDPE/SS biofilms to the fungi environment was done to analyse the biodegradability of the blends. Results showed, MFI of LDPE/SS biofilm decreased as the content of the starch increased as well as the glossiness of the films. The mechanical properties such as tensile strength and elongation also decreased as the starch content increased. However, biodegradability of the films increased as the starch content increased as it can be seen by fungi growth on the surface of LDPE/SS biofilms.

Keywords: Biodegradable films, two-roll mill blending, plastic packaging, and sago starch, low-density Polyethylene.

1.0 Introduction

Plastic materials have gained widespread use in the food, clothing, medical, shelter, transportation, construction and leisure industries due to its feature of strength, lightweight, easily processable and energy efficient. Petrochemical based plastics such as polyolefin, polyesters and polyamides have been increasingly used as packaging materials because of their availability in large quantities at low cost and favorable functionality characteristics such as good tensile and tear strength, good barrier properties to oxygen and aroma compounds and heat seal ability [1]. However, these plastics are made of petroleum-based materials that are not readily biodegradable. These synthetic plastics such as polyethylene and polypropylene have a very low water vapor transmission rate and most importantly, they are totally non-biodegradable, and therefore lead to environmental pollution, which pose serious ecological problems. Polyolefin are not degraded by microorganisms in the environment, which contributes to their long lifetime of hundred of years. There has been an increased interest in enhancing the biodegradability of synthetic plastics by blending them with low cost natural biopolymers.

Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation. They are defined as plastics with similar properties to conventional plastic but

* Corresponding author: Tel.: 07-5535516; Fax: 07-5581463; Email: roshafima@fkkksa.utm.my

which can be decomposed after disposal to the environment by the activity of microorganism [1,2]. Biodegradation occurs when microorganism such as bacteria and fungi degrade a polymer in an aerobic and an anaerobic environment. Carbon dioxide, methane and other natural products are derived from the degradation process. Hence, biodegradation can be stated as the conversion of the constituents of a polymer to carbon dioxide/methane, microbial cellular components and miscellaneous by-products, by microorganisms [2]. Microorganisms break down the polymer chains and consume the material through several methods.

One of the viable alternatives to accelerate the attack of microorganisms to LDPE is the addition of natural polymers; like starch, to guarantee at least a partial biodegradation. Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Starch satisfies the requirements of having adequate thermal stability with minimum interference of melt properties and negligible disturbance of product quality and has been considered as a material candidate in certain thermoplastic applications because of its known biodegradability, availability and low cost [3,4].

In Malaysia, the most abundant starch is sago starch that is harvested from pith sago. Sago starch prepared from the pith of several genera of palms in a form of small whitish, pinkish or brownish grains is mainly for foodstuffs, stabilizers in pharmaceuticals, papers, textiles and plywood.[5] This starch also indicates potential biodegradable fillers for thermoplastics as a new uses of sago. However, due to its poor melt processability, the properties of LDPE/starch blends decreased significantly. The addition of plastifying agent; mainly glycols will enhance the compatibility of LDPE/sago based blend system and is also usually susceptible to microbial attack [6]. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened polymer. Plasticizers also reduce the brittleness of the film by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules and increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular volume [1,6].

The excellent physical properties of polyolefin make them suitable as packaging and film materials. Polyethylene (PE) blended with starch is already found to be a potential candidate to replace non-degradable thermoplastics in the areas of packaging. Films of polyethylene/starch blends with and without vegetable oils as a compatibilizer were prepared using blow film extrusion machine [7]. The degradation of the films under thermo oxidative treatment, ultraviolet light exposure, high temperature, high humidity and natural ambience (soil burial) were increased. It also can be seen that vegetable oil as an additive has a dual role; as a plastizer, it improves the film quality; as a prooxidant, it accelerates degradation of the film. In this paper, an attempt has been made to obtain partially biodegradable LDPE/ sago starch biofilm via melt blending process and its mechanical, morphology and biodegradability characteristics are investigated.

2.0 Materials and Methods

2.1 Materials

The LDPE matrix used in this study was provided by Titan Polyethylene (Malaysia) Bhd, graded as 260 that is used for blown film. Sago starch as filler used in this study was food grade stuff. This food grade starch was a fine white powder with moisture content about 14%.

This starch was oven dried at 100°C for 5-8 hours to reduce its moisture contents to approximately 1% or until the weight of material became constant. Reagent grade glycerol as a plastifying agent has been used in this blending.

2.2 Preparation of LDPE/Starch Blends

The well-dried sago starch (SS) and glycerol were incorporated into the LDPE and melt blending using two-roll mill at 150°C for 10 minutes. Those materials were thoroughly premixed inside a high-speed mixer for 5 minutes before blending. The blended samples were then pressed in ordered to form a film using hot and cold press machine at 150°C, under pressure of 1.2 kPa for 10 minutes. Further, the film samples were cut into uniform shaped specimens according to ASTM D882-02.

2.3 Melt Flow Index (MFI) Measurements

Melt flow index (MFI) of various sample formulations was measured by using Extrusion Plastometer according to ASTM D1238-01. A load of 2.16 kg and temperature at 190°C was used in this measurement.

2.4 Gloss Test

Using ZLR 1050 Glossmeter, this optical property was conducted at angle, 60°. Ten reading were recorded for each formulation and the average value were tabulated.

2.5 Mechanical Test

The tensile strength, elastic modulus, and elongation at break of sample films were determined by using tensile testing machine, Lloyd. The films were cut out into uniform shaped according to ASTM D882-02. The test was carried out at a crosshead speed of 50 mm/min. At least five samples were tested for each formulation.

2.6 Water Absorption Test

Test samples of the various formulations were cut into 1 cm x1 cm. Each sample was weighed prior to immersion in distilled water. Thereafter, the surfaces were wiped dry, re-weighed, and calculated for the percentage of water absorption. Results were recorded every 3 days for 21 days. Five samples were used for each formulation and the average was determined. The percentage of water absorption was calculated according to equation 2.1:

$$\% M_t = \frac{W_s - W_o}{W_o} \times 100 \quad \text{Eq. 2.1}$$

where, M_t = total water absorption, W_s = weight of sample after immersion in water, W_o = original weight of sample before immersion.

2.7 Biodegradability

In this test method, sample films was inoculated with *Aspergillus Niger* (*A. Niger*) on a medium and incubated at surrounding temperature (25°C-37°C) for 21 days [8,9]. Samples

were cut (2.5cm x 2.5cm) and faced on the surface of mineral salts agar in a petri dish containing no additional carbon source. Before placing the samples, agars surfaced were cultivated with *A. Niger* from the tapioca slices. The samples were weighted prior to inoculation with *A.Niger*. Thereafter, the films was examined for evidence of colony growth and reweighed to determine the weight loss.

3.0 Results and Discussion

3.1 Melt Flow Index (MFI) Measurement

Table 1 shows the MFI values of LDPE/SS composites decreased as the content of starch increased. Reduction in MFI values indicates the viscosity of composite increased. This is similar to most filled thermoplastic and in agreement with that reported by researchers before, stating that the MFI of starch composite decreased as the filler loading increased [10]. The reduction may be due to the starch granules that can still retained their shape and functioned as rigid particulate fillers when processed.

When starch content increases, the interaction among the granules was increased; subsequently the spaces between particle-particle became small. If the particle-particle interactions are stronger than particle-matrix interaction, agglomeration of particles may occur and result in the immobilization of more matrix molecules. The matrix molecules become trap in filler particles as the size of agglomerates increases and flows of matrix have been confined. Decreasing of MFI is also due to the fact that starch particles are more viscous than LDPE. This can be observed from the data above; MFI of neat LDPE is higher than LDPE/SS10. However, the decline of MFI was being balanced by incorporation of glycerol. Glycerol as plasticizer decreased the intermolecular forces between polymer coils and increased the molecular spaces [6,11] and mobility of polymers resulted in the increase in MFI.

3.2 Gloss test

The control of surfaces gloss is very important in order to achieve the desired visual effect. The gloss level is determined by the degree of specular reflection [12].

Table 1 MFI value of blends

Materials	Weight percent (wt%)	MFI value (g/10min)
LDPE	100	2.664
LDPE/Gly	99/1	3.1576
LDPE/S10	90/10	1.9236
LDPE/Gly/SS10	89/1/10	2.5787
LDPE/Gly/SS20	79/1/20	1.8029
LDPE/Gly/SS30	69/1/30	1.5937
LDPE/Gly/SS40	59/1/40	1.1816
LDPE/Gly/SS50	49/1/50	0.9197

Table 2 shows the measurement level of glossiness of neat LDPE and LDPE/SS blends with various compositions. In this study, all of the formulations were categorized as semi gloss except for LDPE/GLY/SS50 that was leveled as eggshell. Incorporation of starch into films attributed to the decrease in glossiness indicating that the starch granules influence the glossiness effect. As the starch content is increased, the glossiness is reduced.

Table 2 Measurement level of glossiness

Materials	Angle, 60°	Gloss level [11]
LDPE	41.1 ± 2.92	Semi gloss
LDPE / Gly	43.8 ± 2.28	Semi gloss
LDPE /SS10	32.6 ± 5.02	Semi gloss
LDPE/Gly/ SS10	31.8 ± 7.59	Semi gloss
LDPE/Gly/ SS20	30.1 ± 3.65	Semi gloss
LDPE/Gly/ SS30	28.8 ± 2.19	Semi gloss
LDPE/Gly/ SS40	27.0 ± 2.77	Semi gloss
LDPE/Gly/ SS50	22.8 ± 1.06	Egg shell

3.3 Mechanical Test

Incorporation of sago starch had adversely affected the mechanical properties by reducing the tensile strength and elongation at break, while modulus is increased, as starch content increases as shown in Figure 1. There were two possibilities of the reduction of tensile strength and elongation at break; weakness of interfacial adhesion in which probably attributed to hydrophilic nature of starch, and its in compatibilities with hydrophobic polymers, and less effective cross sectional area of LDPE matrix toward spherical particulates starch granules as the starch contents rose. These observations were in agreement with the results presented by researchers [10,13].

The increased in modulus was suggested because as starch content is increased, filler-filler interaction becomes more pronounced than filler-matrix interaction. Another able to possibility for the high modulus was due to the fact that starch granules were not melting and retain their shape as rigid filler during processing. As the starch contents increases, particles were crowded and reduced the particle-matrix interaction. The films became more rigid and stiffer than films without starch. Starch granules are stiffer than the LDPE matrix in which they are dispersed [14].

3.4 Water Absorption

Observation of starch content over the water absorption for LDPE/starch blends indicated that the moisture uptakes of composites increases up to 9% water absorption with starch contents and immersion times as shown in Figure 2. The results seem to agrees with that reported by researchers that moisture uptake increased with immersion time and increasing filler concentrations [4,6,15].

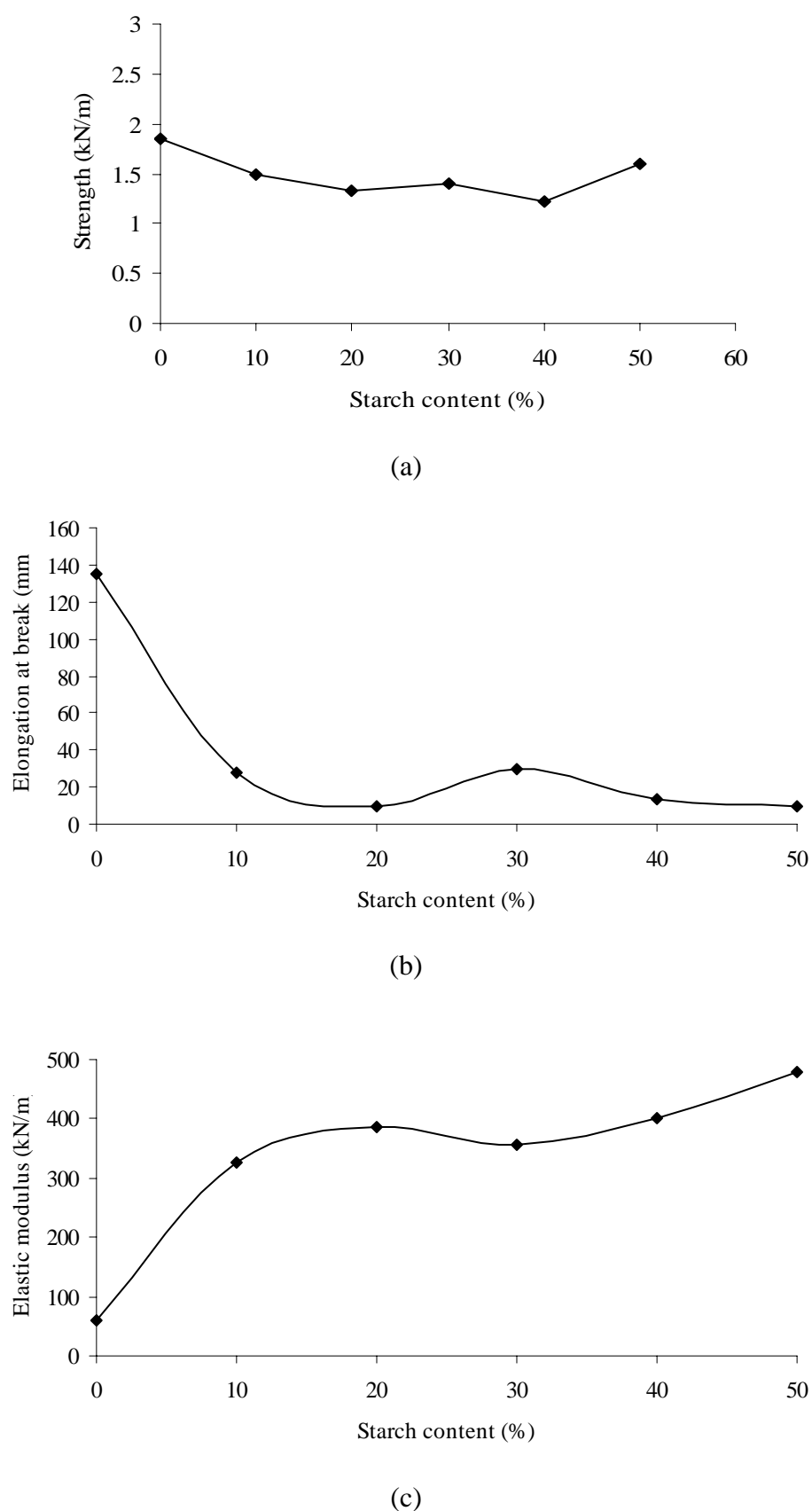


Figure 1 Mechanical properties for LDPE/starch blends: (a) tensile strength, (b) elongation at break and (c) elastic modulus

Starch based synthetic materials tend to absorb water because the hydroxyl group in starch can form a hydrogen bond with water [6,16]. Therefore, as starch contents increases, the tendency to attract water molecules is increased. Over the first 3 days the percentage of water absorption increases progressively. Water penetrated into the films and bonded to the hydroxyl group of starch caused the starch granules to swell and reduce the gap between their molecules and space of the matrix molecules. As the immersion time increases, the gap became smaller and narrower, thus, inhibit the water molecules difficult to diffuse in and rate of water uptake is reduced.

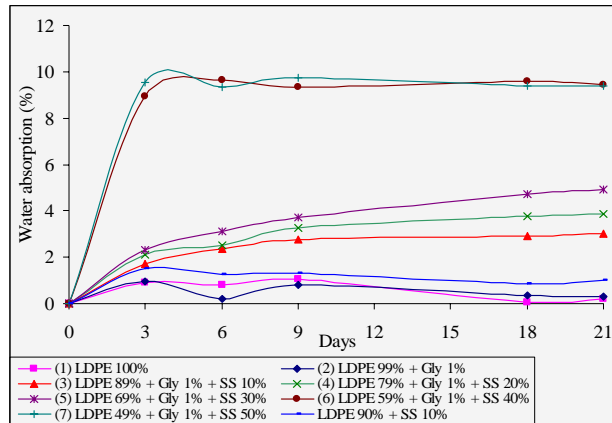


Figure 2 Variation in water uptake of LDPE/SS blends with time of immersion

3.5 Biodegradability Study

Table 3 shows the rating of fungal growth for neat LDPE and various compositions of LDPE/SS blends. From the result, it shows there was no fungi growth on the surface of neat LDPE and LDPE/Glycerol (GLY) as can be seen in Figure 4(a) and 4(b). This is due to microbial resistance behavior presence in LDPE. LDPE are form by carbon-carbon (C-C) linkages in which these linkages are not susceptible to microbial attack [3].

Table 3: Assessment of fungi growth for each formulations of LDPE/starch blends

Materials	Rating* of fungal growth
LDPE	0
LDPE/GLY	0
LDPE/SS10	1
LDPE/GLY/SS10	1
LDPE/GLY/SS20	1
LDPE/GLY/SS30	2
LDPE/GLY/SS40	3
LDPE/GLY/SS50	3

*Rating: 0- no growth apparent, 1-growth clearly visible under microscope, 2-growth covering less than 25% of specimen surface, 3-growth covering more than 25% of the specimen surface

In contrast, after 21 days, the fungi growth was clearly visible under microscope for LDPE/starch content 10% and 20% of starch as shown in Figure 5(a) and 5(b). Starch loading up to 20% shows the apparent fungi growth as rated in the Table 3 and Figure 5(c), 5(d) and 5(e). At 50% sago starch contents (Figure 5(e)), most of the specimen surface was covered by fungi growth. This indicated that the growth of *A. Niger* colony increases as the starch content is increased. The granular starch present on the surface of the polymer film is attacked by fungi. This weakens the polymer matrix and increases the surface volume ratio, hydrophilic and permeability of the film [3].

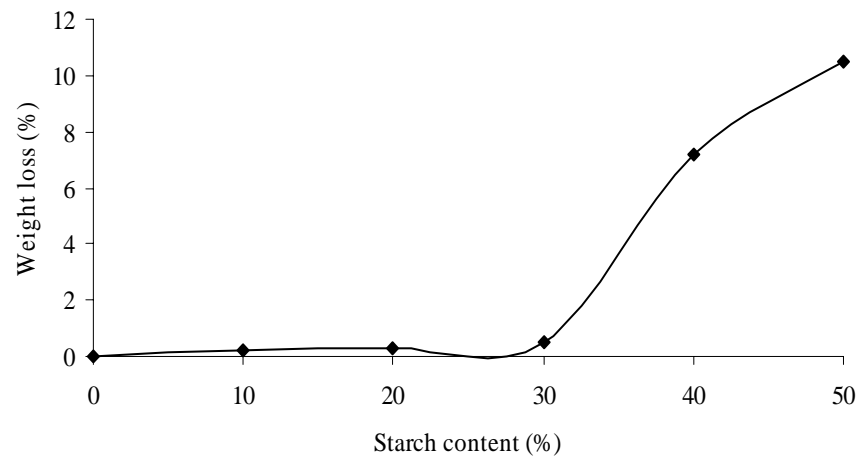


Figure 3. Percentage of weight loss over 21 days of inoculated with *A. Niger*

4.0 Conclusion

In general, we can conclude that addition of sago starch in LDPE is a good way to increase the biodegradability of the LDPE. As the content of sago starch increased, most of the LDPE/SS specimens' surfaces were covered by fungi growth. This indicated that the growth of *A. Niger* colony increases as the starch content increased. Increasing the starch content also increases the water absorption but affect the mechanical properties adversely. Tensile strength and elongation at break are reduced as the starch contents increases. MFI and glossiness of LDPE/SS biofilms also decreased as the starch content increased.

Acknowledgements

The authors would like to thank Universiti Teknologi Malaysia and Polymer Engineering Department for the laboratory facilities and technical support and also supplier for providing the materials.



(a) Pure LDPE (No fungi growth)

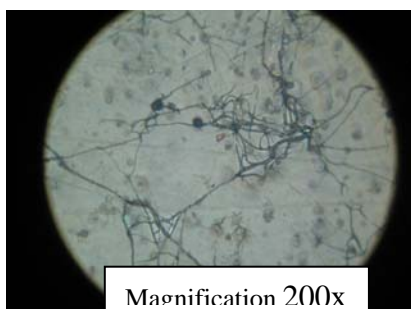


(b) LDPE/GLY (No fungi growth)



(c) LDPE/SS10 (Fungi growth – *A. Niger*)

Figure 4. Evidence of fungi growth (*A. Niger*) on surface of LDPE films with and without starch under microscope magnification 200X.

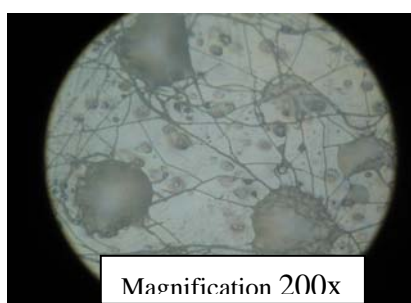


Magnification 200x



No Magnification

(a) LDPE/SS10



Magnification 200x



No Magnification

(b) LDPE/SS20

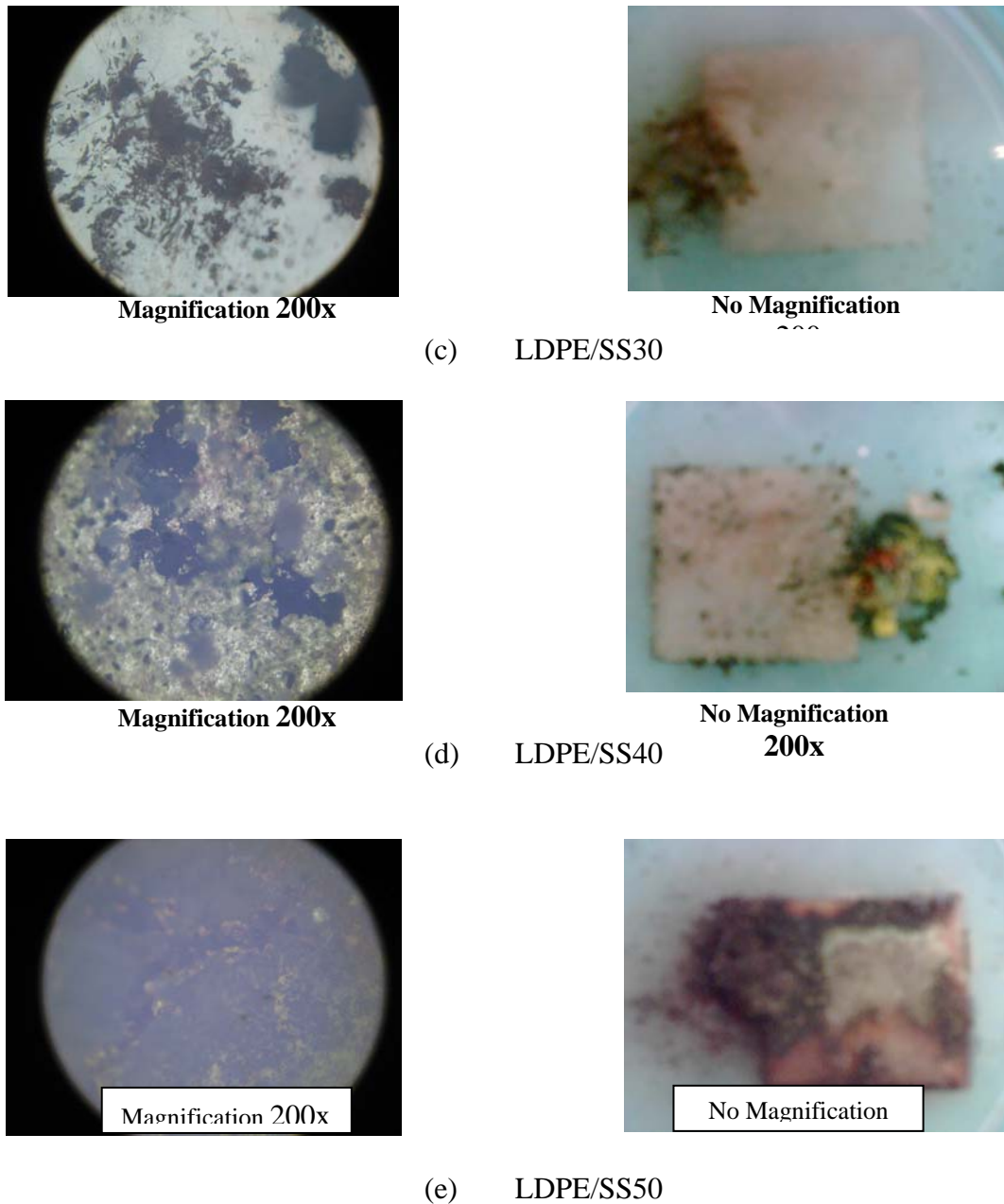


Figure 5. Visual of fungi growth covering surface of LDPE/SS biofilms as the increasing of starch content.

References

- [1] Tharanathan, R.N. 2003. Biodegradable Films and Composite Coatings: Past, Present and Future. *Trends in Food Science & Technology*. 14: 71-78.
- [2] Raghavan, D. 1995. Characterization of Biodegradable Plastics. *Polymer-Plastic Technology Engineering*. 34(1): 41-63.
- [3] Shah, P.B., S. Bandopadhyay, and J. R. Bellare. 1995. Environmentally degradable starch filled low density polyethylene. *Polymer Degradation and Stability*. 47: 165-173.
- [4] Mani, R. and M. Bhattacharya. 1998. Properties Injection Moulded Starch/Synthetic Polymer Blends-III. Effect of Amylopectin to Amylase Ratio in Starch. *European Polymer Journal*. 34(10): 1467-1475.
- [5] Abd-Aziz, S. 2002. Review; Sago Starch and Its Utilization. *Journal of Bioscience and Bioengineering*. 94(6): 526-529.

- [6] Mali, S., L. S. Sakanaka, F. Yamashita and M. V. E. Grossman. 2005. Water Sorption and Mechanical Properties of Cassava Starch Films and Their Relation to Plastisizing Effect. *Carbohydrate Polymer*. 60(3): 283-289.
- [7] Sastry, P. K., D. Satyanarayana and D. V. Mohan. 1998. Accelerated and Environmental Weathering Studies on Polyethylene-Starch Blends Film." *J Applied Polymer Sci*. 70: 2251-2257.
- [8] Chandra, R. and R. Rustgi. 1998. Biodegradable Polymers. *Prog. Polym. Sci*. 23: 1273-1335.
- [9] Akaranta, O., G. E. Oku. 1999. Erratum to Some Properties of Cassava Mesocorp Carbohydrates-Low Density Polyethylene Blends. *Carbohydrate Polymers*. 39: 89-91.
- [10] Thakore, I.M., S. Iyer, A. Desai, A. Lele, and S. Devi. 1999. Morphology, Thermochemical Properties, and Biodegradability of Low Density Polyethylene/Starch Blends." *Journal of Applied Polymer Science*. 74: 2791-2802.
- [11] Audic, J.L. and B. Chaufer. 2005. Influence of Plastisizers and Crosslinking on The Properties of Biodegradable Films Made from Sodium Caseinate. *European Polymer Journal*. 41: 1934-1942.
- [12] Saias, D. ed., (1986). *Plastic finishing and Deration*. New York: Van Nostrand Reinhold Company.
- [13] Ahamed, N.T., R. S. Singhal, P. R. Kulkarni, D. D. Kale and M. Pal. 1996. Studies on Chenopodium Quinoa and Amaranthus Paniculatas Starch as Biodegradable Fillers in LDPE Films. *Carbohydrate Polymers*. 31: 157-160.
- [14] Nawang, R., I. D. Danjaji, U. S. Ishiaku, H. Ismail, and Z. A. Mohd Ishak. 2001. Mechanical Properties of Sago Starch-Filled Linear Low Density Polyethylene (LLDPE) Composites. *Polymer Testing*. 20: 167-172.
- [15] Danjaji, I.D., R. Nawang, U. S. Ishiaku, H. Ismail, and Z. A. Mohd Ishak. 2002. Degradation Studies and Moisture Uptake of Sago-Starch Filled Linear Low-Density Polyethylene Composites. *Polymer Test*. 21: 75-81.
- [16] Pedrosa, A. G., D. S. Rosa. 2005. Mechanical, Thermal and Morphological Characterization of Recycled LDPE/Corn Starch Blends. *Carbohydrate Polymers*. 59: 1-9.